

**SREE NARAYANA COLLEGE, CHATHANNUR**  
**Third Semester M.Sc. Chemistry Model Examination – 2022**  
**INORGANIC CHEMISTRY III**

Time: 3 Hrs

Max. Marks: 75

**SECTION A**

Answer **two** among (a), (b) and (c) from each. Each sub question carries 2 marks

1. (a) Represent diagrammatically the dative bonding seen in metal-cyano complexes.  
(b) Give an example each for a hexahapto ligand and a heptahapto ligand.  
(c) Verify whether  $[\text{IrBrCO}(\text{PPh}_3)_2]$  obeys 18 electron rule or not.
2. (a) List the factors that affect the stability of coordination compounds.  
(b) What is meant by trans effect?  
(c) What is the Kurnakovs test?
3. (a) Give two examples for metallo-enzymes containing iron.  
(b) Briefly discuss the coordination environment of the metal ion in Vitamin  $\text{B}_{12}$ .  
(c) Explain the mechanism of oxygen binding in haemocyanin.
4. (a) Explain doppler broadening with an example.  
(b) What is superhyperfine splitting in esr spectra?  
(c) How many signals are obtained in the  $^{19}\text{F}$  nmr spectra of the following  
(i)  $\text{SF}_6$       (ii)  $\text{SF}_4$       (iii)  $\text{XeOF}_4$ . Give reasons for your answer
5. (a) List any two differences between GM counter and Proportional counter.  
(b) Distinguish between half life and average life. How are they related?  
(c) Summarise the liquid drop model of the nucleus.

[2 × 10 = 20]

**SECTION B**

Answer either (a) or (b) from each question. Each sub question carries 5 marks

6. (a) IR spectroscopy provides vital information in during the study of metalcarbonyls. Explain.  
(b) Discuss the characteristics of oxidative addition and reductive elimination reactions of organometallic compounds.
7. (a) Give an account of the photochemical reactions of complexes.  
(b) Using  $[\text{PtCl}_4]^{2-}$  as the starting material, how can the cis and trans isomers of  $[\text{PtCl}_2(\text{NH}_3)(\text{PPh}_3)]$  and  $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]^-$  be prepared
8. (a) Explain the role played by calcium in blood clotting.  
(b) Briefly discuss nitrogen fixation.
9. (a) Discuss the application of ESR spectroscopy to Cu (II) complexes.

(b) Discuss the utility of Mossbauer spectroscopy in the study of complexes of iron.

10. (a) Give a brief note on nuclear shell model

(b) What is meant by radioactive equilibrium? The ratio between atoms of two radioactive elements A & B at equilibrium was found to be  $3.1 \times 10^9:1$ . If the half life period of A is  $2 \times 10^{10}$  years what is the half life of B.

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Construct the MO diagram of dibenzene chromium and explain the bonding using MOT.

12. What are inner sphere and outer sphere reactions? Explain the salient features.

13. Discuss in detail the function of PS-I and PS-II in photosynthetic activity.

14. How is CD and ORD employed in the structure determination of metal complexes?

15. Explain the principle involved in the working of the reactors in nuclear power plants

[10 × 3 = 30]

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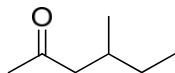
Time: 3 Hrs

Max. Marks: 75

**SECTION A**

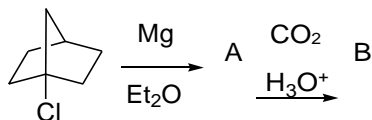
Answer **two** among (a), (b) and (c) from each. Each sub question carries 2 marks

- What is the effect of solvent polarity on  $n-\pi^*$  transition?
  - How will you distinguish between Intramolecular hydrogen bonding and intermolecular hydrogen bonding using IR spectroscopy?
  - Predict the fragmentation pattern of the following molecule

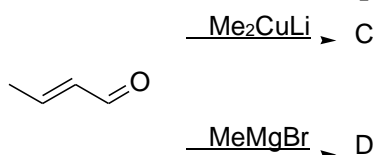


- How many peaks do you expect in the nmr spectrum of N,N-dimethyl formamide? Explain.
  - How does the coupling constant differ between a geminal and vicinal hydrogens?
  - What are shift reagents? Give an example

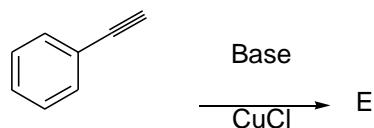
- Complete the reaction



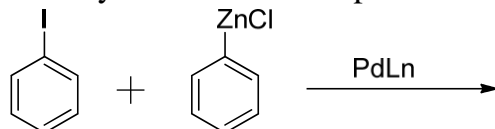
- Predict the structure of the products C and D in the reaction given below



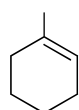
- Write the structure of the compound E in the reaction given below



4. (a) Identify the reaction and predict the product

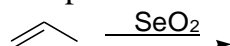


- (b) Suggest a retrosynthetic route for the following compound

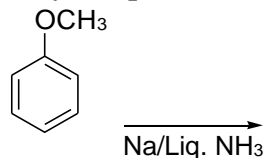


- (c) Give any two protecting groups for hydroxyl group.

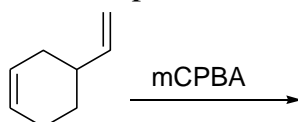
5. (a) Complete the reaction



- (b) Identify the product in the reaction given below



- (c) What is the product obtained in the following reaction?

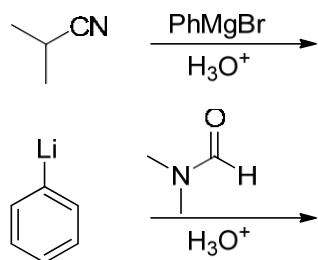


[2 × 10 = 20]

### SECTION B

Answer either (a) or (b) from each question. Each sub question carries 5 marks

6. (a) Discuss the principle and applications of MALDI.  
 (b) Give the mass fragmentation pattern of toluene and phenol.
7. (a) Explain the anomaly in the chemical shift value of acetylene and benzene.  
 (b) Write on any two 2D NMR technique.
8. (a) Complete the following reaction and suggest a suitable mechanism
- BrCC(=O)OCC + CC(=O)C >> [Zn, Benzene, Reflux]
- (b) Predict the product (s) of the following reactions with mechanism



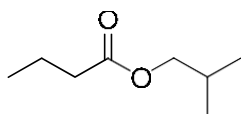
9. (a) Convert benzaldehyde to ethylbenzene using umpolung strategy.  
 (b) Discuss the mechanism for Stille coupling with the help of an example.
10. (a) Illustrate Sharpless asymmetric epoxidation with the help of an example.  
 (b) Give a brief outline of four Cr(VI) reagents used for oxidation reactions.

[5 × 5 = 25]

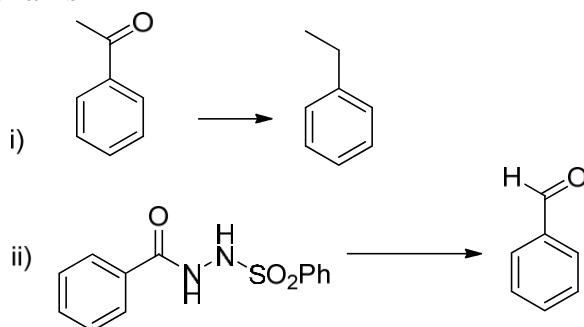
### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. a) Discuss the mass spectral fragmentation pattern of aromatic compounds, ketones and amides.  
 b) Write on FAB.
12. a)  $^1\text{H}$  NMR spectrum of a compound gives the following spectral data.  $\delta$ 9.78(1H, s), 7.75(2H, d), 6.90(2H, d), 3.8(3H, s). Identify the compound  
 b) Discuss DEPT nmr of



13. a) Discuss the preparation and reactivity of Tebbe's reagent.  
 b) Illustrate the synthetic utility of silyl carbanions using examples
14. a) Discuss Suzuki and Heck coupling with the help of mechanism.  
 b) Write in brief on olefin metathesis
15. a) Comment on the reactivity of various bulky metal hydrides using suitable examples.  
 b) How will you bring about the following conversion? Suggest a suitable mechanism



[10 × 3 = 30]

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**PHYSICAL CHEMISTRY III**

Time: 3 Hrs

Max. Marks: 75

**SECTION A**

Answer **two** among (a), (b) and (c) from each. Each sub question carries 2 marks

1. (a) Arrange  $O_2$ ,  $O_2^+$ ,  $O_2^-$  in the increasing order of stability. Justify your answer.  
(b) Write briefly about 'Perturbation theory'.  
(c) Write the Hamiltonian for He atom and suggest a suitable trial wave function for it.
2. (a) Predict and justify the condition at which a real gas obeys the following equation of state  $PV = RT + Pb$ .  
(b) The van der Waals constant  $a$  for two gases are  $4.17$  and  $0.024 \text{ dm}^6 \text{ atm mol}^{-2}$  respectively. Explain which is easily liquefiable and why?  
(c) At what pressure does the mean free path of argon gas at  $25^\circ\text{C}$  become comparable to the diameter of the atoms themselves? Given  $\sigma = 0.36 \text{ nm}^2$ .
3. (a) The shift in frequency shown by a proton from TMS is  $180 \text{ Hz}$ , when measured on a  $100 \text{ MHz}$  instrument. Calculate the chemical shift in ppm.  
(b) Calculate the ESR frequency of an unpaired electron in a magnetic field  $0.33 \text{ Tesla}$ . Given for free electron  $g=2$ ,  $\beta=9.273 \times 10^{-27} \text{ J/T}$ .  
(c) Explain the basic principle of X-ray photo electron spectroscopy.
4. (a) Apply phenomenological equation in thermal diffusion.  
(b) How is temperature influence the miscibility curve of a three-component system forming one pair of partially miscible liquids?  
(c) What are the conditions under which linear relations are valid to understand irreversible processes?
5. (a) How do parameterization techniques help to reduce the task of computation?  
(b) Construct the  $z$ -matrix of  $CO_2$  molecule.  
(c) Differentiate STO and GTO.

[2 × 10 = 20]

**SECTION B**

Answer either (a) or (b) from each question. Each sub question carries 5 marks

6. (a) Calculate the first order correction to the energy levels for a one dimensional box with a slanted bottom whose potential energy varies as

- $v_x/a$  where  $a$  is the length of the box.
- (b) Apply HMO theory to butadiene molecule and discuss the molecular orbitals and their corresponding energy levels.
7. (a) Calculate  $C_v$  for the following gases at room temperature.  
 i) He                    ii) HCl                    iii) CO<sub>2</sub>  
 Discuss the principle of equipartition of energy.  
 (b) Which among CO<sub>2</sub> and O<sub>2</sub> undergo effusion faster. Justify your answer.
8. (a) Write a brief account of NMR spectroscopy.  
 (b) Discuss the application of Mossbauer spectroscopy.
9. (a) Derive expressions for entropy production in the case of system contains both the matter flow and current flow.  
 (b) Verify the Onsager reciprocal relation in the case of simple chemical reaction A : B.
10. (a) Write a note on non-quantum mechanical method of energy calculation.  
 (b) What is potential energy surface? Explain its significance.

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Discuss the bonding in H<sub>2</sub> molecule by valence bond theory.
12. Discuss about the transport properties of gas. Show that the ratio of thermal conductivity to that of coefficient of viscosity =  $C_v/M$
13. a) Explain the principle and applications of NQR spectroscopy.  
 b) When N<sub>2</sub> gas is excited with radiation of energy 21.22 eV from a helium lamp, electrons are ejected with kinetic energies 5.63eV and 4.53 eV. What are their binding energies?

(7+3)

14. a) Draw the phase diagram of a three-component liquid system with three pairs of partially miscible liquids. Explain.  
 b) How would you understand (i) thermo osmosis and (ii) thermal diffusion from irreversible thermo dynamics?

(5+5)

15. a) Write briefly on ab-initio methods used in computational chemistry? What are the merits and demerits of the method?  
 b) Explain the terms i) force field ii) contracted Gaussians.

(7+3)

[10 × 3 = 30]

